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New Type of Halogen Bond: Multivalent Halogen Interacting with π- and σ-Electrons

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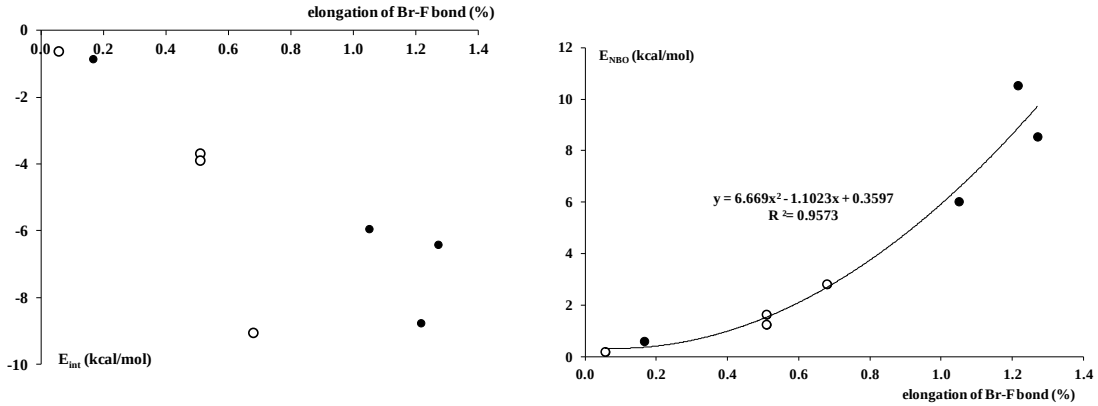
Abstract: MP2/aug-cc-pVTZ calculations were performed for complexes of BrF_3 and BrF_5 acting as Lewis acids through the bromine centre with species playing a role of Lewis base: dihydrogen, acetylene, ethylene and benzene. The molecular hydrogen donates electrons by its σ-bond while in remaining moieties - in complexes of hydrocarbons, such an electron transfer follows from π-electrons. The complexes are linked by a kind of the halogen bond that is analyzed first time in this study, i.e. it is the link between the multivalent halogen and π or σ-electrons. The nature of such halogen bond is discussed as well as various dependencies and correlations are presented. Different approaches are applied here, the Quantum Theory of Atoms in Molecules, Natural Bond Orbital method, the decomposition of the energy of interaction, the analysis of electrostatic potentials, etc.

Keywords: electron charge shifts; halogen bond; octet rule; hydrogen bond; σ-hole bond



(a) (b)

Figure S1. The relationships between the elongation of the equatorial Br-F bond (percentage elongation in relation to this bond in the isolated BrF_3 or BrF_5 species) and (a) the interaction energy (corrected for BSSE); (b) the NBO energy expressing orbital-orbital interactions. Black circles correspond to the BrF_3 complexes while white ones to BrF_5 complexes.

Table S1. The equatorial (Eq) and axial (Ax) Br-F bond lengths for the BrF_3 and BrF_5 species; these bond lengths in complexes and in isolated moieties are presented in the table (all values in Å).

Complex	Eq(complex)	Ax(complex)	Eq(monomer)	Ax(monomer)
BrF_3-H_2	1.813	1.720	1.810	1.720
BrF_3-C_2H_2	1.829	1.730	1.810	1.720
BrF_3-C_2H_4	1.833	1.738	1.810	1.720
BrF_3-C_6H_6	1.832	1.737	1.810	1.720
BrF_5-H_2	1.767	1.702	1.766	1.702
BrF_5-C_2H_2	1.775	1.701	1.766	1.702
BrF_5-C_2H_4	1.775	1.702	1.766	1.702
BrF_5-C_6H_6	1.778	1.708	1.766	1.702

Table S2. The coordinates (in Å) of atoms′ positions for optimized complexes that are analyzed here are presented below; MP2/aug-cc-pVTZ level.

BrF_3-H_2

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	35	0.000000	0.193347	0.000000
2	9	-1.773223	-0.188527	0.000000
3	9	1.808872	0.301879	0.000000
4	9	0.232020	-1.511295	0.000000
5	1	-1.509261	2.697637	0.000000
6	1	-0.899767	3.116691	0.000000

BrF_3-C_2H_2

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	35	0.000000	-0.304547	0.000000
2	9	1.826015	-0.412208	0.000000
3	9	-1.826005	-0.411821	0.000000
4	9	-0.000183	-2.034275	0.000000
5	6	0.607783	2.599957	0.000000
6	6	-0.607559	2.599851	0.000000
7	1	1.671884	2.592514	0.000000
8	1	-1.671662	2.592521	0.000000

BrF_3-C_2H_4

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	35	0.359279	0.000539	0.000107
2	9	0.479496	1.829685	0.000150

3	9	0.450945	-1.830285	0.000156
4	9	2.096862	-0.013335	-0.000447
5	6	-2.491388	-0.663599	-0.000187
6	1	-2.484169	1.239496	-0.923907
7	6	-2.486238	0.677048	-0.000177
8	1	-2.484407	1.239119	0.923772
9	1	-2.493171	-1.226203	0.923341
10	1	-2.492973	-1.226547	-0.923518

BrF_3-C_6H_6

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	35	1.025207	-0.000009	0.107003
2	9	1.174003	-1.824613	0.050677
3	9	1.174096	1.824594	0.050689
4	9	2.578867	-0.000039	-0.670701
5	6	-1.600715	0.698343	1.201413
6	6	-1.909352	1.397741	0.032194
7	6	-1.601141	-0.700867	1.199997
8	6	-2.223969	0.699327	-1.131343
9	1	-1.887238	2.478837	0.029491
10	6	-1.910188	-1.397693	0.029366
11	1	-1.357032	-1.243863	2.104128
12	6	-2.224389	-0.696731	-1.132753
13	1	-2.458159	1.240784	-2.038300
14	1	-1.888741	-2.478796	0.024473
15	1	-2.458911	-1.236204	-2.040807
16	1	-1.356347	1.239351	2.106669

BrF_5-H_2

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	35	-0.032177	-0.001490	0.201292
2	9	1.362878	-1.037295	0.522354
3	9	-1.301150	1.036365	-0.460554
4	9	0.564964	0.011494	-1.392368
5	9	0.998164	1.419816	0.404460
6	9	-0.935892	-1.418376	-0.342798
7	1	-2.396370	-0.185030	2.490677
8	1	-2.678097	0.129149	1.884257

BrF_5-C_2H_2

Center	Atomic	Coordinates (Angstroms)

Number	Number	X	Y	Z
1	35	0.255077	0.035434	-0.021914
2	9	0.812467	1.720202	0.007678
3	9	0.040901	-1.728423	0.002295
4	9	1.897993	-0.334332	0.221178
5	9	0.679023	-0.058734	-1.741660
6	9	0.184433	0.045889	1.748166
7	6	-2.987288	0.744106	-0.149521
8	6	-2.934288	-0.464256	-0.046900
9	1	-3.047867	1.801914	-0.237823
10	1	-2.883706	-1.522631	0.044440

BrF_5-C_2H_4

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	35	0.323966	0.000209	-0.064463
2	9	0.489938	1.766203	0.005428
3	9	0.481847	-1.766226	0.012294
4	9	-0.178264	0.004600	1.639056
5	9	1.165618	-0.004849	-1.627357
6	9	1.897248	-0.002134	0.584489
7	6	-2.877159	-0.667363	-0.203654
8	1	-3.154169	1.230086	-1.087905
9	6	-2.876756	0.669154	-0.206044
10	1	-2.606515	1.231115	0.678127
11	1	-2.607214	-1.226354	0.682485
12	1	-3.154896	-1.231270	-1.083510

BrF_5-C_2H_6

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	35	-0.815661	0.000028	-0.000036
2	9	-1.017798	-1.249033	-1.249700
3	9	-1.017822	1.249099	1.249618
4	9	-2.523170	0.000131	-0.000158
5	9	-1.017998	-1.250061	1.248570
6	9	-1.017628	1.250145	-1.248674
7	6	2.095189	1.207823	0.699540
8	6	2.093923	-0.001941	1.395551
9	6	2.095468	1.209680	-0.696112
10	6	2.094801	-1.209851	0.696322
11	1	2.079901	-0.003381	2.477428
12	6	2.094492	0.001776	-1.395346

135	13	1	2.081419	2.147057	-1.236016
136	14	6	2.095092	-1.207988	-0.699331
137	15	1	2.080200	-2.147222	1.236218
138	16	1	2.080935	0.003221	-2.477228
139	17	1	2.080724	-2.143917	-1.241731
140	18	1	2.080906	2.143756	1.241933